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New Amended Specification

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**Title: MULTIWALL PERMREACTOR AND SEPARATOR PROCESSES FOR
FUEL CELLS AND POWER APPLICATIONS**

The amended specification contains no new matter

Date: November 1, 2002

TITLE OF THE INVENTION

MULTIWALL PERMREACTOR AND SEPARATOR PROCESSES FOR FUEL
CELLS AND POWER APPLICATIONS

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CROSS REFERENCE TO RELATED APPLICATIONS

Continuation in part of Ser. No. 08/595,040, now U.S. Patent 6,090,312 (Jul. 2000)

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

Not Applicable

REFERENCE TO A "SEQUENCE LISTING," A TABLE, OR A COMPUTER PROGRAM LISTING APPENDIX SUBMITTED ON COMPACT DISC

Not Applicable

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

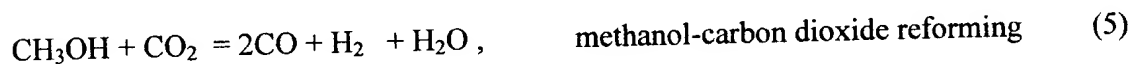
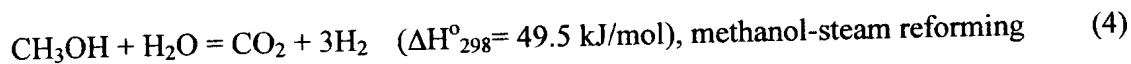
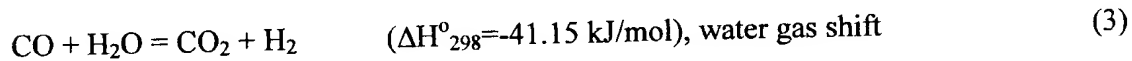
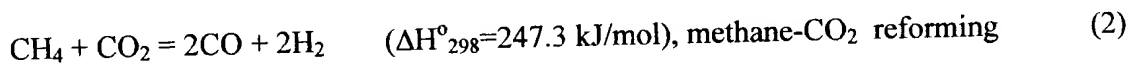
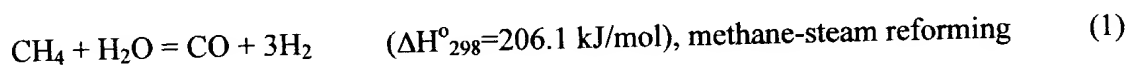
1. This invention relates to new process designs referring to double wall or multiwall type permeable reactors (so called double wall permreactors or double wall membrane reactors) and to consecutive separators, including membrane type and cryogenic separators, for conducting the hydrocarbon-steam reforming, hydrocarbon-carbon dioxide reforming, combined hydrocarbon-steam and -carbon dioxide reforming, alcohol-steam reforming, alcohol-carbon dioxide reforming, and combination of these carbon based fuel conversion reactions for production of valuable upgraded hydrogen rich gas fuels. The

invention also relates to the utilization of the end reaction products such as pure hydrogen and synthesis gas (hydrogen and carbon monoxide, hydrogen and carbon dioxide mixtures), and mixtures of these, into specific applications of consecutive fuel cells, gas engines and gas turbines by application of uniquely presented process configurations.

2. DESCRIPTION OF THE RELATED ART INCLUDING INFORMATION DISCLOSED UNDER 37 CFR 1.97 AND 1.98

2 The current invention describes new and improved processes which involve double wall or multitube permeable reactors (multitube permreactors, multitube membrane reactors) and downstream separators for the hydrocarbon-steam reforming, hydrocarbon-carbon dioxide reforming, combined hydrocarbon steam and carbon dioxide reforming, alcohol steam reforming, alcohol carbon dioxide reforming and combination of these previous reactions. Methane is considered a primary hydrocarbon feedstock in the processes.

3 The reactions and heats of reactions that are referred to and utilized within the embodiments of the invention are well known and are listed below:



4 The aforementioned are catalytic reactions utilizing active metals as catalysts in monometallic, bimetallic, or multimetallic metal compositions. The catalysts are

supported on inorganic oxides such as on various types of alumina and enriched with earth metal additives to enhance catalytic activity and feedstock conversion and minimize deposition of carbon on active metal sites and loss of activity.

5 Use of related processes involving catalytic reactor with downstream permeator configurations and systems of those were disclosed in our previous US patent # 6,090,312 (July 2000). Use of these reactor-separator systems increase the overall process efficiency by increasing the total conversion of feedstocks such as the following:

natural gas, landfill gas, biomass gas, coal gas, hydrocarbons, hydrocarbons-carbon dioxide mixtures, methane, methane-carbon dioxide mixtures, methanol and higher alcohols. Moreover, the yields to hydrogen and carbon monoxide or hydrogen and carbon dioxide are increased by the use of the integrated membrane type permeators which separate effectively the H_2 and CO_2 gas constituents out of the exit reformed streams. Process efficiency is further improved by the recycling of unreacted and non-separated (non-permeated) hydrocarbons (e.g., methane) and carbon monoxide into the first (primary) reactor (reformer) or by the alternative direction of the same streams into a consecutive catalytic reactor (reformer or water gas shift reactor) for additional production of hydrogen and carbon dioxide. Direct utilization of the produced and separated hydrogen, synthesis gas, and hydrogen-carbon dioxide mixtures from these processes into consecutive synthesis reactors, fuel cells, gas turbines and gas engines are additional advantages and continuing applications and utilizations of the disclosed processes.

6 Current invention elaborates on the introduction and specification of double and multiwall type membrane reactor processes (double and multiwall permreactor processes) related to the above reactions which can be implemented accordingly, as described below.

7 A specific problem in parallel gas reaction and separation within microporous membrane reactors (permreactors) is the lack of selective separation for the target compound (e.g., hydrogen) in certain materials. Thus, microporous inorganics and composites materials allow the permeation through the membrane of not only the targeted compound but also of other reaction products and reactants that compete for permeation based on their molecular diameter or molecular weight. This effect, separates in the permeate of the membrane reactor a stream which is not pure but needs further separation in order to be utilized as a pure compound (e.g., hydrogen pure gas for synthesis or fuel). Therefore, capital and operation costs are increased when a single wall membrane reactor process of the above structure is to be used. The introduced double and multiwall permreactor process solves this problem by applying a second consecutive membrane which only separates the targeted compound and offers a highly pure separated product. For hydrogen separation as an example, a second metal or metal alloy membrane can be used, placed after the first microporous membrane, as described below.

8 The described permreactors wherein the processes are occurring, are designed to consist of interconnected parts which can be readily taken apart, cleaned, serviced and assembled when service or maintenance is necessary. For the disclosed integrated reaction-separation systems specific applications are disclosed such as the utilization of the end products and/or of the permeated (separated) streams into consecutively placed hydrogen driven fuel cells, gas turbines and gas engines.

9 Previous reactor and permeable reactor (membrane reactor) designs from the above cited references refer mainly to methane and methanol steam reforming reactions but not to carbon dioxide reforming, and combined steam and carbon dioxide reforming, as the present invention does. Also, present invention applies to higher carbon atom hydrocarbons and alcohols feedstocks for the occurring reactions. Moreover, previous inventions refer to processes occurring within a single reactor or permreactor or other reaction vessel instead of reactor-separator systems as the present invention additionally describes. Present invention introduces processes which are based on double wall and extended on multiwall permreactors for conducting conversion-upgrading reactions of primary and secondary hydrocarbon and alcohol mixtures. The processing multiwall permreactors can be of various designs and the walls be made by various appropriate materials as disclosed within the embodiments and claims of the invention. These catalytic permreactors are adapted to specific process requirements in terms of setting values of key operating variables such as reaction temperature, pressure, space velocity, feed composition, catalyst composition and weight, in order to deliver final products (such as hydrogen and synthesis gas) in the required purity and throughput for the consecutive applications. Selection of such variables like temperature, pressure, and feed composition in the different compartments of the described membrane reactor system is also of significant importance. This is because an interconnection and synergetic activity between the various compartments occurs during operation, with reaction and separation operations to occur at the same time. Moreover, flexibility in the selection of the double wall permreactor materials such as metals, inorganics, polymers, and composites, allows for the design of processes which separate and deliver specific species (such as specific

gases) with the required purity and throughput to the consecutive applications. Flexibility in the selection of functional and specific permreactor wall materials for each process operation have also economic advantages. Therefore, the selection of less expensive membrane materials and manufacturing techniques for a specific permreactor, permeator and overall process is available with the current invented designs and will affect (reduce) the cost of the overall process operation.

10 Present invention also teaches the direct utilization of end product streams to consecutive fuel cells, gas turbines and gas engines. Use of such low pollution energy systems with increased efficiency is of renewed interest in utility, energy, chemical, refinery, automobile and environmental companies. Present invention focuses on converting and upgrading primary hydrocarbon feedstocks such as methane, natural gas, coal gas, refinery feedstocks such as naphtha, alcohol feedstocks such as methanol, ethanol and higher alcohols into the higher calorific value hydrogen and carbon oxide mixtures. Also, it focuses on converting secondary, flue, and waste hydrocarbon feedstocks such as acidic natural gas, biomass and sewage gas, flue gas rich in CO_2 and CH_4 to same valuable end products. Therefore, present invention describes also environmentally benign processes which upgrade and abate at the same time waste type gases and effluents to valuable hydrogen, synthesis gas, and hydrogen-carbon dioxide mixtures. The in situ conversion of carbon dioxide containing hydrocarbon mixtures to alternative fuels and chemicals including hydrogen and carbon monoxide, and the subsequent mitigation of carbon dioxide's negative atmospheric and terrestrial greenhouse effects are considered additional benefits from the implementation of this invention.

BRIEF SUMMARY OF THE INVENTION

11 The present invention discloses processes which consist of double wall and multiwall permreactors and systems of such advanced reactors with consecutively placed separators and reactors to perform specific process operations. These integrated chemical and mechanical systems offer operational advantages by conducting in-situ reactions, in comparison with single wall permeable reactors and conventional impermeable reactors. Consequently, different double wall permreactor processes are disclosed for the catalytic hydrocarbon and alcohol reforming reactions.

The first process comprises of a double wall permreactor which incorporates three concentric hollow cylindrical tubes with the two inner ones to be made by permeable (and permselective) inorganic, composite, polymer, or metal materials depending on the type of feedstocks used, the reactions and reaction conditions occurring, and the desired composition of the final exit streams. Heating tubes run through the most-inner cylinder which is also filled with the main catalyst to conduct the appropriate reaction. Additional catalyst can be placed in the two outer annular spaces created between far outer and next inner and between next inner and most inner tubes. By varying the catalyst position and catalyst type this process can be applied to a number of different reactions.

Similarly, the second process involves a double wall permreactor which consists of three concentric hollow cylindrical tubes with the two inner ones to be made by permeable (and permselective) inorganic, composite, polymer or metal materials and with the catalyst for the main reaction to be contained in the annular space between the far outer and the next inner cylindrical tubes. Heating in this process is applied into the

external side of the far outer tube. By applying catalyst at the different annular spaces created between the concentric tubes, this process can be applied to various reactions. The two processes differ in the heat and mass transfer profiles and distribution across the radial and axial distances. Use of the described advanced permreactor processes offer significant increases in conversion of reactants and increases in yield and selectivity of products. This is achieved via improved mass and heat transfer, and improved reaction rates within the defined reaction and catalyst zones as described above. Also, the effect of removing products out of the defined reaction zones during the reaction increases the reactant conversion and the yield to useful products by shifting the equilibrium of the occurring reactions to the product side. Further, use of the described permreactors allows for systems of reactions to take place and be combined in the same module. Synergetic effects of utilizing products and/or reactants of these reactions to conduct improved processes in a consecutive and/or parallel manner is also a result of this invention.

12 Moreover, this invention pertains to combined processes of the described permreactors with consecutive permeators and reactors for further separation and processing of the post-reaction gases exiting from the permreactors. This is especially useful in low conversion permreactors where postprocessing of exit gases is necessary. Permeators can be made by polymer, composite or metal membranes for the downstream concomitant separation of hydrogen and carbon dioxide gases, or for the separation of only hydrogen. These permreactor-permeator systems are applied to combined hydrocarbon steam and carbon dioxide reforming, hydrocarbon-steam reforming,

hydrocarbon-carbon dioxide reforming, alcohol steam and carbon dioxide reforming. The processes are capable to increase the reactant conversion and the yield to hydrogen, carbon monoxide, and carbon dioxide. The separated hydrogen and carbon oxides can be consumed in consecutively placed fuel cells, gas turbines and gas engines.

13 The invention also includes hydrocarbon and alcohol carbon dioxide-steam reforming process which consists of permreactors with cryogenic separators wherein the consecutive cryogenic separators replace the membrane permeators. This process also applies to low conversion permreactors, and a pure mixture of hydrogen and carbon monoxide is recovered as a final product from the separation step. The permreactors as described above can be directly interconnected with solid oxide and molten carbonate fuel cells for using the product hydrogen, carbon monoxide, and unreacted steam as direct fuel in the anode of the fuel cell or by using the permeated hydrogen as fuel in anode. This is especially useful for high conversion permreactors wherein most of the exit gas is product. Similarly, the hydrogen rich gas product can be consumed in consecutive placed gas type engines, turbines, and combined cycle plants.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

14a Fig.1, shows a vertical cross sectional view of a concentric double wall cylindrical process permreactor with tubular type heaters located along the inner main catalyst zone, consisting of an inner membrane tube and an outer membrane tube enclosed within a far outer impermeable tube.

14b Fig.2, shows a sectional view of the same process permreactor as in Fig.1, including the three catalyst beds, the two cylinder type inner and outer membrane tubes,

the inner axial heating elements, and the inlet and outlet ports in each section of the permreactor.

14c Fig.3, shows multiple double wall process permreactors of those described in Fig.1, but without the far outer impermeable tube, which are placed symmetrically inside a larger common impermeable metal tube, to create a multiple tube permreactor with a common external area for collecting final permeate hydrogen.

14d Fig.4, shows a cross section of a similar concentric double wall process permreactor, consisting of a far outer and heated impermeable tube, a next inner membrane tube and a most inner membrane tube:

14e Fig.5, shows multiple double wall process permreactors of those described in Fig.4, which are placed symmetrically inside a larger impermeable metal tube, to create a multiple tube permreactor with a common external heating area.

In the Figures below, the permreactors can be any of those described in Fig.1, Fig3, Fig.4, and Fig.5 above.

14f Fig.6, shows a combined process which includes a catalytic permreactor in series with a consecutive permeator or a reactor for hydrocarbon and alcohol steam and carbon dioxide reforming, or for hydrocarbon-carbon dioxide reforming only. The reject from the permeator stream containing non-permeate hydrocarbon and carbon monoxide can be optionally fed into a consecutive catalytic steam reforming reactor.

14g Fig.7, shows a catalytic permreactor-permeator process for the hydrocarbon or alcohol steam reforming reaction. The reject from the membrane permeator hydrocarbon, alcohol, and carbon monoxide stream can be recycled into the initial reformer or fed into a consecutive (second) steam reforming reactor.

14h Fig.8, shows a process of a catalytic permreactor which combines a consecutive cryogenic separator for hydrocarbon and alcohol steam and CO₂ reforming or for hydrocarbon, alcohol CO₂ reforming only reactions. The liquified stream separated from the cryogenic separator, containing hydrocarbon, CO₂ and steam can be fed into the inlet of the initial reforming reactor. The gaseous stream from the separator contains H₂ and CO.

14i Fig.9, shows a process which includes a catalytic permreactor for hydrocarbon and alcohol steam and CO₂ reforming or hydrocarbon CO₂ reforming only with complete conversion of hydrocarbon and carbon dioxide gases into products. The final H₂ and CO product mixture is fed directly into a consecutive or integrated SOFC (solid oxide fuel cell) or MCFC (molten carbonate fuel cell) unit for continuous electricity generation.

DETAILED DESCRIPTION OF THE INVENTION

15 Fig.1 shows the top cross section of the double wall processing permreactor used in steam and carbon dioxide reforming of hydrocarbons and alcohols. It consists of a concentric double membrane wall cylindrical assembly with tubular type heaters located within the catalyst, along the most inner main catalyst zone. A far outer impermeable tube (7) nests the two permeable concentric tubes (1) and (2). Reacting feedstocks such as steam and hydrocarbons or CO₂ and hydrocarbons or steam, CO₂, hydrocarbons and alcohols, are fed within the main catalyst zone (4) through special inlet fittings and react in the catalyst to produce hydrogen, carbon monoxide, carbon dioxide. Primary feedstocks for reforming are methane and methanol. Optionally, small volumetric quantities of hydrogen can be added into above feedstocks to prevent the deactivation of catalyst in the inlet of the reactor, wherein propensity for hydrocarbon cracking into

steam and hydrocarbons or CO_2 and hydrocarbons or steam, CO_2 , hydrocarbons and alcohols, are fed within the main catalyst zone (4) through special inlet fittings and react in the catalyst to produce hydrogen, carbon monoxide, carbon dioxide. Primary feedstocks for reforming are methane and methanol. Optionally, small volumetric quantities of hydrogen can be added into above feedstocks to prevent the deactivation of catalyst in the inlet of the reactor, wherein propensity for hydrocarbon cracking into carbon is high in absence of hydrogen. The hydrocarbon reforming catalysts can be nickel, ruthenium, rhodium, palladium, chromium and cobalt, enriched with earth type metals such as lanthanum, potassium, magnesium, cerium, yttrium, calcium, and supported on oxides of alumina (Al_2O_3), titania (TiO_2), silica (SiO_2), zirconia (ZrO_2), lanthanum (La_2O_3), types of glass. Methanol reforming catalysts can be zinc, chromium, copper, iron, nickel and cobalt enriched with and supported on similar metal and metal oxides. These catalysts are also used in the catalytic processes described in the next embodiments (figures).

16 The reactant pressurized gas is fed into the main catalytic zone (4) and the pressure in this zone is maintained at the highest. The pressure drops progressively from zone (4) to zone (8) to zone (5), with outer zone (5) to be at the lowest pressure. The pressure gradient is necessary to maintain an outward permeation and flow of the selective gases radially from membrane (2) to membrane (1). Hydrogen is first removed along the most inner membrane tube (2), wherein the membrane material is inorganic or composite. Carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols may also permeate through first membrane (2) in a lesser degree than hydrogen. An inert carrier gas such as argon, nitrogen, steam or a mixture of these gases may also flow along the

permeate annulus, between tubes (2) and (1), through suitable inlet fittings to carry the permeate components at a fixed pressure. Permeate hydrogen is further removed via permeation along the next inner membrane tube (1), so that final permeated stream contains pure hydrogen only which can be consumed in fuel cells and gas turbines and engines. Next inner membrane tube (1) is made by a metal or non-porous inorganic membrane which allows only hydrogen to permeate through, and therefore purifies hydrogen from the permeating carbon oxides, steam, alcohols and hydrocarbons, which flow in the annular zone between the two membrane tubes.

17 Metal materials permeable to hydrogen for next inner membrane tube (1) include palladium, vanadium, palladium alloys such as palladium-nickel, palladium-silver, palladium-copper, palladium-tungsten. Hydrogen permeable non-porous inorganic membranes include silicon carbide, silicon nitride, tungsten carbide, tungsten nitride, titanium carbide, titanium nitride, tantalum carbide, tantalum nitride. Porous and microporous inorganic membranes make the most inner tube (2) which include oxides of alumina, silica, titania, zirconia, various types of glass. Composite type membranes for tube (2) are made by deposition or fabrication of a metal or inorganic material into a porous inorganic substrate (support) to make it hydrogen or hydrogen and carbon oxide selective. Inorganic membrane materials are made or modified via various deposition techniques including incipient wetness, dip coating and sol gel methods.

Metal and metal alloys for next inner tube (1) are also deposited on porous inorganic or metal surfaces to make them hydrogen selective. Palladium and other metal deposited membranes are fabricated by electroless plating, electroplating, sputtering, chemical

vapor deposition, physical vapor deposition and other applicable metal deposition or metallization techniques.

18 Organic polymer, composite, or copolymer membranes are made by polymers such as polyimides, polycarbonates, polysulfones, polybenzimidazoles, polyphosphazenes, polyamides, polystyrenes, polycaprolactams, parylenes, polyvinyl halides, polyacetates, polysiloxanes and others in order to be permeable to hydrogen or to both hydrogen and carbon dioxide. Composites of materials are made as hydrogen or hydrogen and carbon dioxide permeable membranes and are based on inorganic-metal, inorganic-polymer, inorganic-metal-polymer composites. Metal, metal alloys, non-porous inorganic, membranes are highly selective to hydrogen, while porous and microporous inorganic, polymer, and composite membranes are selective also to other species including carbon dioxide. The disclosed double wall permreactor process can utilize among the aforementioned materials to satisfy the necessary process requirements. The described membranes (1), (2) can also act as catalytic materials to partly catalyze the occurring reforming reactions.

19 The external space, created between the next inner membrane tube (1) and the impermeable far outer shell (7), which receives the final permeate hydrogen, can be either empty, or may optionally contain a selective catalyst (5) which converts the permeate hydrogen after its combination with another flowing component.

20 Permeation of reaction products through the membrane tubes, especially this of hydrogen through the most inner membrane tube (2), shifts the thermodynamic equilibrium conversion of reactant species towards the product side and produces excess hydrogen and carbon oxides within the catalytic reaction zone (4). Next inner membrane

21 As an alternative to the invented process and design, at low operating gas reforming temperatures (e.g., between 200-500°C) and in absence of steam as reactant, the most inner membrane tube (2) is made by inorganic or composite materials and the next inner membrane tube (1) is made by inorganic, composite, or high temperature polymer materials (i.e., materials with high glass transition temperature, T_g) which are permselective to both hydrogen and carbon dioxide gases. These two gases permeate through the next inner tube (1) as they flow along the central annular zone (8) after permeation from the most inner membrane (2). The recovered mixture of H_2 and CO_2 is used as a direct feed in a molten carbonate fuel cell via the overall electrochemical reaction:

$$H_2 + CO_2 + 1/2 O_2 \rightarrow H_2O + CO_2$$

22 The external (next inner) membrane (1) serves also as a backup membrane medium in case the most inner membrane (2) develops cracks or defects and its permeability to various gases increases substantially. In this case, the next inner membrane (1) will selectively separate specific gases including hydrogen based on the selected membrane materials as described above. Moreover, operational and maintenance service for replacing old or damaged membrane tubes and catalysts become easier with the proposed design, because the parts of the permreactor are interconnected properly via top and bottom caps and can be disassembled and assembled accordingly. The top and bottom ends where the tubes are interconnected are sealed with proper materials or welded or glazed to prevent gas flow or leak between the various compartments.

23 An optional design of the permreactor may include an additional catalytic zone (8) which is created between the most inner membrane tube (2) and the next inner membrane tube (1) and can be used in various reactions and processes. Heating of the reformer or

reactor is achieved via cylindrical tubes (6) arranged symmetrically around the axial reactor axis and operated in the gas combustion regime by flowing waste type hydrocarbons or hydrocarbon-hydrogen mixtures mixed with oxygen or air. Part of unreacted hydrocarbons, alcohols, carbon monoxide and non-permeate (rejected) hydrogen or any mixture of these species from the catalytic reformer outlets (4), (5), (8) can be recycled as well into heating tubes (6). Flue or waste gases coming out from the interconnected fuel cells, engines or turbines can also be used directly to provide the necessary heat content in tubes (6).

24 Fig.2, shows a lateral sectional view of the process permreactor described in Fig.1. The embodiment includes catalyst beds 4, 5 and 8 placed along the different tubular sections of the permreactor. The most inner tube bears inner membrane (2) while next inner tube bears outer membrane (1). The most inner tube includes tubular heating elements A6 along its axial length. Feedstock gases are entered into the permreactor via inlet ports A1 and the product and reactant gases exit via outlet ports A3. Alternative safety outlets A5 are located in the outer shell to discharge excess pressure in case of a sudden increase. Top and bottom caps A2 and A4 close the inlet and outlet of the tubular permreactor system and seal properly the ends of the different tubes by means of proper fittings or by using seal or glaze type materials or welding to prevent unwanted gas flow or leaks between the tubes.

25 Fig.3, shows multiple double wall process permreactors of those described in Fig.1, after removal of the far outer impermeable tube (7), which all are placed symmetrically inside a larger impermeable tube (A1), to create a multiple tube reactor with a common external area for collecting final permeate hydrogen. The common

external area may optionally contain a catalyst (zone 5) wherein a catalytic reaction is conducted as described in Fig.1 above. This type of process configuration is able to process large amounts of reacting feedstocks and to produce larger throughputs of hydrogen rich mixtures in comparison with the single module process of Fig.1.

In an optional process, the multitube array shown in Fig.3 is enclosed effectively within a circular or cylindrical solid oxide fuel cell which has as anode the surrounding inner cylindrical solid oxide surface. The hydrogen emitted from zone (5) in the multiple reforming tubes is consumed directly by the surrounding SOFC anode for continuous electricity generation. The flue hot gas emitted by the fuel cell is used directly in endothermic heating of heating tubes (6).

A similar process is defined when both H_2 and CO_2 permeate in zone (5). In this case a cylindrical molten carbonate fuel cell is utilized which consumes the binary mixture in the cylindrical anode which surrounds the multitube array of the reformers. The two processes are applied as well with a single permreactor as described in Fig.1, which is surrounded by the cylindrical solid oxide or molten carbonate fuel cell.

26 Fig.4 shows the top cross sectional view of another developed double wall membrane process reactor (permreactor) used in the process of steam and carbon dioxide reforming of hydrocarbons and alcohols. The overall permreactor process consists of a most outer hollow impermeable tube (outer shell) (1) which nests two more concentric hollow permeable tubes, a next inner one (2) and a most-inner (3). Most outer cylinder (1) is made by an impermeable metal or metal alloy such as stainless steel. Next-inner membrane tube (2) is made by an inorganic or composite material which is permeable and selective to hydrogen and partly to other reaction species as well.

27 The derived concentric multitube assembly has proper inlet and outlet fittings for feeding the feedstocks and discharging the post-reaction species similar to those described in Fig.1 and Fig.2 above. Inlet and outlet fittings are connected into the ends of the three different tubular cylinders similarly to those shown in Fig.2, to deliver and collect gases flowing through these spaces. Top and bottom caps are also used to seal the ends of the overall reactor. Before the caps are applied and tighten, the annular space between the different cylinders is filled with the appropriate reforming catalyst in pellet or particle form to make the catalytic reaction zones (4), (5) and (7). Catalysts used in reforming reactions are same with those mentioned above in embodiment of Fig.1. The pressure is higher in zone (4) and drops progressively inwards from zone (4) to zone (7) to zone (5), with zone (5) to be at lowest pressure. The pressure gradient assures the selective permeation and flow of gases inwards from membrane (2) to membrane (3).

28 In steam, CO_2 reforming of hydrocarbons and alcohols, hydrogen is removed along the next-inner lateral membrane surface (2), with carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols to partly permeate also through the same membrane in lesser degree than hydrogen, depending on the type of the membrane material used. An inert carrier gas such as argon, nitrogen, steam or a mixture of those gases, may flows along the permeate annular zone, between tubes (2) and (3), through the inlet fittings, to carry the permeate components at a specific pressure value. Permeate hydrogen is further removed through permeation along the lateral surface of most-inner membrane tube (3) so that final permeate stream contains pure hydrogen only, with pure hydrogen to be used in various subsequent applications including feed to fuel cells, gas turbines and engines.

29 The most-inner membrane tube (3) is made by a metal or non-porous inorganic membrane which allows only hydrogen to permeate through and therefore purifies the hydrogen from the permeating carbon oxides, steam, hydrocarbons and alcohols, flowing along the central annular zone (7). The membranes in tubes (2) and (3) are made with similar manufacturing techniques as those described in embodiment of Fig.1. Membranes (2) and (3) can act also as catalysts to partly catalyze the occurring reactions. The most-inner membrane tube can be either empty or may contain a selective catalyst (5) which can convert permeate hydrogen after combination with another component flowing through the inner bore of this tube. Pure permeated hydrogen can be used primarily as direct feed in hydrogen driven fuel cells, gas turbines, engines, and combined cycle plants.

30 Permeation of hydrogen through next inner membrane tube (2) shifts the thermodynamic equilibrium conversion of reactant species to the product side and produces excess hydrogen and carbon oxide products in zone (4). Most-inner membrane tube (3) thereby, serves as the final permeable medium for the recovery of highly pure hydrogen for use in hydrogen utilization applications. Most-inner membrane tube (3) serves also as a separation medium for hydrogen out of the central annular zone (7) so that the partial pressure of hydrogen lowers substantially along the annular zone, and thereby continuous driving force exists for permeation of hydrogen from the catalytic reaction zone (4) into the central annular zone (7).

31 As an alternative to the disclosed process and design, for low operating gas reforming temperatures (e.g., between 200-500°C) and in absence of steam as a reactant, the next inner membrane tube (2) can be made by an inorganic or composite material and

the most inner membrane tube (3) can be made by inorganic, composite, or high temperature polymer materials (i.e., a material with high T_g , glass transition temperature) which are permselective to both hydrogen and carbon dioxide gases. These two gases may first permeate through the inner membrane (2) and flow along the central annular zone (7) as they finally permeate through the membrane tube (3). The recovered mixture of H_2 and CO_2 in zone (5) can be used as a direct feed in a molten carbonate fuel cell as described above in embodiment of Fig.1.

32 The most inner membrane tube (3) serves also as a backup membrane in case first inner membrane (2) develops cracks or defects and its permeability to various gases increases substantially. In this case, the most inner membrane (3) will selectively separate specific gases including hydrogen based on the selected membrane materials as described above. Operational and maintenance service for replacing old or damaged membrane tubes and catalysts in the described permreactor become easier with the proposed design, because the parts of the permreactor are interconnected properly via top and bottom caps and can be disassembled and assembled accordingly. The top and bottom ends of the interconnected tubes are sealed, glazed, or welded with proper materials to prevent gas flow and leaks between the various compartments.

33 An optional design of the permreactor may include an additional catalytic zone (7) which is created between the inner membrane tube (2) and the most inner membrane tube (3) and can be used in various reactions and processes.

34 Heating of the described reactor is achieved via heat provision in the external surrounding area (zone 6). The external to the reformer combustion regime can be fueled by flowing waste type hydrocarbons or hydrocarbon-hydrogen mixtures mixed with

oxygen or air. Flue or waste gases coming out from the interconnected fuel cells, engines, turbines can be also used directly to provide the necessary heat in zone (6). Part of the unreacted hydrocarbons, alcohols, carbon monoxide and non-permeate hydrogen, or any mixture of these post-reaction species coming out of the outlets connected with the catalyst zones (4), (5) and (7) can be recycled as well in the external combustion-heating zone (6). Optionally, external heating of most-outer tube (1) can be provided by cylindrical type heaters or heating elements in contact with the outer tube. Thus, the lateral sectional view of the described processing permreactor in Fig.4 is similar with the description in Fig.2 with the exception that there are no tubular type heaters in the most inner annular zone (5) as shown in Fig.1 and Fig.2.

35 Fig.5, shows multiple double wall process permreactors of those described in Fig.4, which all are placed symmetrically, inside a larger impermeable tube (shell) (A1), to create a multiple tube permreactor with a common external heating area (6). The most outer impermeable tubes (1) which consist the external part of the multiple tubes are in direct contact with the common heating zone (6). This type of process configuration is able to process large amounts of reacting feedstocks and to produce larger throughputs of hydrogen rich mixtures in comparison with the single module process shown in Fig.4.

In an optional process, the multitube array as shown in Fig.5 is enclosed effectively within a circular or cylindrical solid oxide fuel cell which has as anode the surrounding inner cylindrical solid oxide surface. The hydrogen emitted from zone (5) in the multiple reforming tubes is consumed directly by the surrounding SOFC anode for continuous electricity generation. The flue hot gas emitted by the fuel cell is used directly in endothermic heating of the common external zone (6).

A similar process is defined when both H_2 and CO_2 permeate in zone (5) via membrane tube (3). In this case a cylindrical molten carbonate fuel cell is utilized which consumes the binary mixture in the cylindrical anode which surrounds the multitube array of the reformers. The two processes are applied as well with a single permreactor as described in Fig.4, which is surrounded by the cylindrical solid oxide or molten carbonate fuel cell.

36 Fig.6, depicts a catalytic permreactor process with a consecutive permeator (or optionally with a second consecutive reactor) and with an optional third consecutive reactor, for conducting catalytic reforming reactions. In Fig.6, stream 1 contains hydrocarbon or alcohol feedstocks such as methane (CH_4), methanol (CH_3OH), higher alkanes (paraffins) or alcohols, naphtha, natural gas, which are mixed with steam and CO_2 and introduced in catalytic permreactor A for conducting simultaneously reactions (1), (2) and (3), or mixed with CO_2 only for conducting reactions (2) and (3). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from hydrocarbon cracking especially in the inlet of permreactor A.

37 Catalytic permreactor A can be any of the permreactors described in the embodiments of Fig.1, Fig.3, Fig.4, and Fig.5 above, with H_2 in the general case to be separated in permeate stream 1b via valve A1. H_2 and CO_2 gases combined can be separated in permeate stream 1b in special applications, if a suitable polymer, inorganic, or composite membrane is used. The rejected exit stream from the permreactor may contain CO product together with unreacted steam, CO_2 , hydrocarbons, alcohols, and non-permeate hydrogen. This becomes stream 2 and enters into a heat exchanger B, wherein the unreacted steam is removed through condensation and by the heat

exchanging process new steam is generated in stream 6 from the water or steam of stream 5. Stream 6, can provide steam in permreactor A and reactor E through streams 9 and 10,18 respectively, in an alternative or continuous manner via use of valves B1 and E1. The steam in stream 6 acquires the exchanged heat load from stream 2, the hot gas effluent of reformer A, and thus its derived streams 9,10,18 can be mixed directly with streams 1 and 12 which are fed directly into reactors A and E respectively.

38 Steam from stream 6 is used via streams 10,18 and valves B1,E1 to provide the initial steam content in reformer E. Stream 7, passes through a bed of particles C (a moisture adsorbent) to remove any non-condensed traces of moisture and through the exit stream 8 enters into membrane permeator D. Stream 8, contains CO product, non-permeate H₂ product, unreacted hydrocarbon (e.g., CH₄) and CO₂ gases and has been cooled at the operating temperature of permeator D. H₂ or both H₂ and CO₂ are removed in permeate stream 11 of permeator D, through the permselective action of a metal, inorganic, polymeric or composite membrane respectively. Non permeating stream 12, containing hydrocarbons (e.g., CH₄), alcohols, CO and CO₂ or hydrocarbons, alcohols, and CO respectively, depending on the type of membrane used in permeator D, exits from vessel D through stream 12 as a reject stream. Stream 12 enters into reformer E for conducting simultaneously reforming and water shift reactions selected from the group of reactions (1), (2) and (3), and is converted into H₂, CO, CO₂ or H₂ and CO₂ only, depending on the feed composition of stream 12 in reformer E. Steam in reformer E is provided via stream 18. Unreacted steam is removed from exit stream 15 by passing this stream through a heat exchanger F. Steam is generated from water or steam of stream 16 and via streams 17,18 and valve E1, the generated steam is fed into the inlet of reformer

E. Exit stream 19 contains H_2 , CO, CO_2 or H_2 , CO_2 products and traces of unreacted hydrocarbons, depending on the operating conditions, that is the temperature, pressure, space velocity and feed composition of streams 12 and 18, of reformer E.

39 If conversion is high in permeable reformer A under certain operating conditions, the product in stream 2 is mainly CO and H_2 which can be used directly as fuel for power generation in solid oxide or molten carbonate fuel cells, gas turbines and engines.

40 If the overall process consists of two reformers and the intermediate permeator, and the final product is a H_2 and CO_2 mixture in exit stream 19, it can be used separately or it can be mixed with stream 11 to make a combined H_2 and CO_2 stream. Alternatively, CO_2 can be condensed cryogenically from the binary mixture and pure hydrogen can be produced. The final hydrogen product can be used for chemical synthesis or as direct feed in fuel cells, gas turbines and engines for power generation applications (e.g., transportation, stationary). Applicable hydrogen driven fuel cells for utilizing the pure separated hydrogen from the process, include proton exchange membrane (PEM), solid oxide (SOFC), molten carbonate (MCFC), alkaline (AFC), phosphoric acid (PAFC) and modifications-combinations of these fuel cells. Generated hydrogen product from streams 1b, 11, and 19 can be combined and used as a single stream in a specific application.

41 The described process is able to overcome the thermodynamic equilibrium limitations of the reactant hydrocarbon (e.g., CH_4) and carbon oxide (e.g., CO_2) conversion, through the removal of H_2 only, or of combined H_2 and CO_2 gases in permreactor A and permeator D. The calorific value of the obtained H_2 , CO product in permreactor A, is higher than this of the reactant hydrocarbon (e.g., CH_4), CO_2 and steam

and the endothermic heat of reaction is stored in the products which can be subsequently used as gas fuels.

42 Assuming 100% conversion in permreactor A for reactions (1) and (2) and equilibrium for reaction (3), then 2 mol of CH_4 (with heat of combustion: 425.6 kcal), 1 mol of CO_2 (with no heat of combustion), and 1 mol of $\text{H}_2\text{O}(\text{g})$ (with no heat of combustion), produce 3 mol of CO (with heat of combustion: 202.8 kcal) and 5 mol of H_2 (with heat of combustion: 341.5 kcal). These are values at 25°C . This corresponds to about 28% increase in calorific value for the products. Endothermic heat can be provided in reformers A and E through the flue or waste hot gases coming out of the interconnected fuel cells, turbines or engines and directed as input streams 3 and 13, as also described in Figs.1, 2, 3, 4, 5 before. Part of the exiting streams 2 and 15 can be also used to heat the reformers. The two reformers can operate at same or different temperature and pressure conditions.

43 In an alternative design, permeator D is replaced by a catalytic reforming reactor D wherein continuous conversion of the rejected reactants occurs from the previous step. In this case, vessels B and C are eliminated and the inlet stream 8 contains unreacted hydrocarbons, alcohols, CO , CO_2 , some H_2 and unreacted steam. Additional steam can be added in stream 8 if necessary for the reforming reaction. The exit reject stream 12 from catalytic reactor D contains mainly H_2 and CO products after the unreacted steam condensation, and is used as synthesis gas fuel in similar applications as described above.

44 Fig.7, is a process embodiment which is related with those described in Fig.6 but with stream 1 to contain hydrocarbon feedstocks such as methane, higher alkanes such as naphtha and natural gas, also alcohol feedstocks such as methanol, ethanol, propanol,

butanol which are mixed with steam only and introduced in catalytic permreactor A filled with catalyst particles to conduct the methane steam reforming reaction (1) and the simultaneously occurring water gas shift reaction (3). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from hydrocarbon cracking especially in the inlet of permreactor A.

45 Catalytic permreactor A, can be any of the permreactor types described in embodiments of Figs.1,3,4,5 above, with H_2 to be separated in permeate stream 1b via valve A1, in the general case. H_2 and CO_2 combined, can be separated in permeate stream 1b in special applications, if a polymer, inorganic, or composite membrane is used in permreactor A. The rejected exit stream from the permreactor may contain product CO_2 , CO, unreacted steam, hydrocarbons, alcohols, and non-permeate H_2 . This becomes stream 2 and enters into heat exchanger B, wherein the unreacted steam is removed through condensation, and by the heat exchanging process new steam is generated in stream 8 from the water or steam of stream 7. Stream 8, can provide steam in permreactor A and reactor E through streams 6 and 10,20 respectively, in an alternative or continuous manner via use of valves B1,E1. The steam in 8 acquires the exchanged heat load from stream 2, the hot gas effluent from permeable reformer A, and thus its derived streams 6,10,20 can be mixed directly with streams 1 and 14 which are fed directly into reactors A and E respectively. Steam from stream 8 is used via streams 10,20 and valve E1 to provide the initial steam in reformer E. Stream 9 passes through a bed of particles (a moisture adsorbent) C to remove any non-condensed traces of moisture and through exit stream 11 enters into membrane permeator D. Stream 11 has been cooled in the

temperature of permeator D and contains CO, CO₂, unreacted hydrocarbons, alcohols and non-permeate H₂ gas.

46 H₂ or both H₂ and CO₂ are removed via permeate stream 12 of permeator D, through the permselective action of a metal, inorganic, polymer or composite membrane. Non permeating stream 13 containing hydrocarbons (e.g., CH₄), alcohols, CO and CO₂ or hydrocarbons, alcohols, and CO respectively, depending on the type of the membrane used in permeator D, exits from permeator D, through the reject stream 13. In case wherein stream 13 contains hydrocarbons, alcohols, and carbon monoxide (CO) it can be recycled via valve D1 and stream 5 into first permeable reformer A for continuous reforming and conversion to main H₂ and CO₂ products. Alternatively, by use of valve D1, stream 13 becomes stream 14 which enters into steam reformer E for additional reforming and shift reactions, (reactions (1), (3)), and conversion to H₂ and CO₂ products. In case wherein stream 13 contains hydrocarbons, CO and CO₂, by use of valve D1, stream 13 becomes stream 14 which enters into modified steam and CO₂ reformer E for additional reforming and shift reactions, via reactions (1), (2) and (3) and conversion into H₂ and CO products.

47 Reformers A and E are endothermic and flue gas streams 3,4 and 15,16 respectively are used to provide the necessary heat content to drive parallel reactions (1), (2) and (3) to completion. The two reformers can operate at same or different reaction temperature and pressure conditions. If conversion is high in permeable reformer A under certain operating conditions, the product in stream 2 is mainly CO₂ and non-permeate H₂ which can be used directly as feed in a molten carbonate fuel cell.

48 If the overall process includes a second conventional reformer E and the intermediate permeator as shown in Fig.9, and the final product is H_2 and CO_2 in exit stream 21, this product can be used separately or it can be mixed with stream 12 to make a combined H_2 and CO_2 stream to be used in similar applications. Alternatively, CO_2 can be condensed cryogenically from the binary mixture and pure hydrogen product can be produced. Final H_2 product can be fed in fuel cells, gas turbines and engines for power generation applications (e.g., transportation, and stationary), same to those described in embodiments of the previous figures. The flue gas streams coming out of the interconnected fuel cells, engines and turbines, are used as streams 3 and 15 to heat the reformers A and E.

49 By providing external heat through flue or waste gas combustion in the reformers or through internal stream recycling and with the described two heat exchangers in place, the energy requirement of the one reactor-one permeator or two reactor-one permeator cascades is fulfilled and these processes operate in a thermally independent manner providing for an energy efficient design. Endothermic heat can be provided also in reformers A and E via the combustion of part of exit or recycled streams from the reaction zone of reformers A and E (streams 2, 17), as also described in Figs.1,2,3,4,5 above.

50 Fig.8, is a new embodiment of a steam and CO_2 hydrocarbon or alcohol reforming process which includes a permeable reformer as described above in Figs.1,3,4,5 followed by a cryogenic separator for separation of certain post-reaction gases exiting from the reject exit of the reformer. In Fig.10, stream 1 is introduced into catalytic permreactor A, containing hydrocarbon or alcohol feedstocks such as methane (CH_4) or methanol

(CH₃OH) mixed with steam and CO₂ for conducting simultaneously reactions (1) through (5), or mixed with CO₂ only for conducting reactions (2), (3), (5). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from methane cracking especially in the inlet of permreactor A.

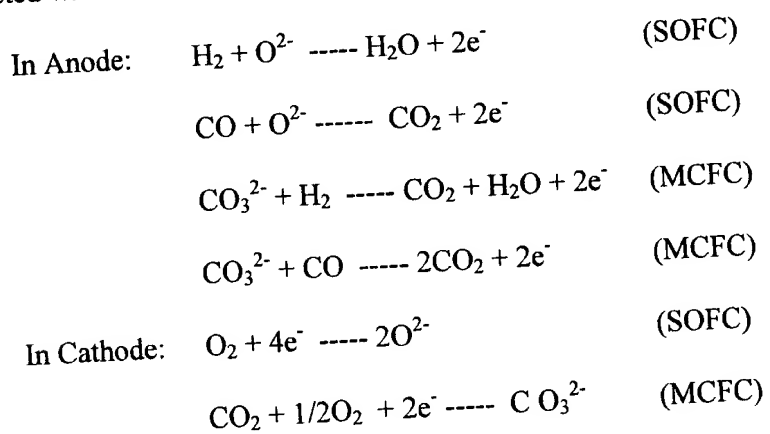
51 Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with H₂ to be separated from the reformer, and exit in permeate stream 1b via valve A1. The rejected exit stream from the permreactor contains product CO together with unreacted steam, CO₂, hydrocarbons, alcohols, and non-permeate H₂. This becomes stream 2 and enters into a steam condenser C wherein the unreacted steam is condensed and by the heat exchanging process new steam is generated in stream 17 from the water or steam of stream 16. Steam through stream 17 is recycled into stream 1 in inlet of reformer A. Stream 5 free of steam, exits from condenser C and enters into cryogenic separator B, which operates at a temperature lower than the boiling temperature of carbon dioxide, hydrocarbons, alcohols so that these compounds are separated easily as liquids and collected in the bottom of the separator. However, the operating cryogenic temperature of separator is higher than the boiling points of carbon monoxide and hydrogen so that these compounds remain in gas phase and exit from the separator as a gas mixture. Liquified components exit via stream 7 through valve B1. Gas phase hydrogen and carbon monoxide exit as stream 6 via valve B2. Liquified stream 7 can be recycled into the feed stream of reformer A (stream 1) via stream 8 after evaporation in evaporator D. Alternatively, stream 7 can be further processed in another reforming reactor by becoming stream 9 which enters into reformer E, for additional steam and CO₂ reforming of any remaining hydrocarbons and alcohols via reactions (1),

(2) and (3). Optionally, steam in reformer E is provided via stream 18 which is a bypass stream of stream 17. Stream 10 exiting the reformer can optionally condense the containing unreacted steam by passing through the heat exchanger F. Steam in stream 12 can be optionally fed into reformer E via valve E1. Stream 13 exiting the heat exchanger F is dry, and contains H_2 and CO as main products with traces of unreacted hydrocarbons, alcohols, and CO_2 depending on the operating temperature and pressure of the reformer E and the composition of feed streams 9 and 12.

52 Recovered H_2 and CO in stream 13 can be either used separately or optionally be combined with stream 6 from the separator to make one stream to be used as fuel in conventional and fuel cell systems or in chemical synthesis. Direct application of the produced H_2 and CO mixture is in gas turbines, engines, and in solid oxide and molten carbonate fuel cells for power generation. Similarly, H_2 recovered in stream 1b, can be used as clean or blending fuel in similar applications. Reformer A can be optionally substituted by a non-permeable reformer A, wherein all catalytically produced H_2 is contained into the exit stream 2. Valve A1 and stream 1b are eliminated and all post-reaction gases exit from stream 2.

53 Fig.9, is a modified embodiment of the process described in Fig.3, Fig.5, and Fig.6. It applies to a complete conversion of hydrocarbons (e.g., CH_4), or alcohols (e.g., CH_3OH), CO_2 , and steam reactants of stream 1, within the permeable reformer A, into H_2 and CO products. The occurring reactions are (1) through (5). Catalytic permreactor A, can be any of the types described in embodiments of Figs. 1,3,4 and 5 above, with H_2 only or H_2 and CO_2 combined to be separated in permeate stream 3 via valve A1 depending on the type of membranes used in A. The exiting from the permreactor, reject

stream 2, containing only CO and non-permeating H₂, or CO, non-permeating H₂, and traces of unreacted steam, enters into a solid oxide (SOFC) or molten carbonate (MCFC) fuel cell which is the unit B. Stream 2 is directed in the anode of the fuel cell, and makes the fuel constituent of the fuel cell. Stream 4 consists of O₂ or air for SOFCs, and of CO₂-O₂, or CO₂-air mixtures for MCFCs respectively, and is directed in the cathode of the fuel cell B. Stream 4 is therefore the oxidant, for the known electrochemical reactions conducted within the two different cells for electric current generation:



54 Optionally, part of hydrogen from permeate stream 3, can be fed into stream 2, via bypass stream 3b, to adjust the composition of H₂ in stream 2 to that required to feed the fuel cell B. Stream 7 which is the flue hot gas from the fuel cell, can be directed as stream 5 to make the hot heating gas of reformer A to provide the necessary endothermic heat content in A.. Reformer A can be optionally substituted by a non-permeable reformer A, wherein all catalytically produced H₂ is contained into the exit stream 2. Valve A1 and streams 3 and 3b are eliminated and all post-reaction gases exit from stream 2. Fuel cell B still operates with the same function as described above with flue gas stream 7 from the fuel cell to heat the reformer A.

In an alternative process configuration of Fig.9, the H_2 and CO_2 permeate binary mixture from stream 3 can be fed directly in a molten carbonate fuel cell. In another alternative configuration of Fig.9, the permeate pure H_2 from stream 3 can be fed directly in any hydrogen driven fuel cell such as solid oxide, molten carbonate, alkaline, phosphoric acid proton exchange membrane types to provide fuel for a continuous cell operation.